

**EVALUATION OF FERROELECTRIC MATERIALS FOR POWER PLANE  
DECOUPLING CAPACITORS AT FREQUENCIES ABOVE 1 GHZ**

Period August 1, 1993 to July 31, 1995

**FINAL REPORT**

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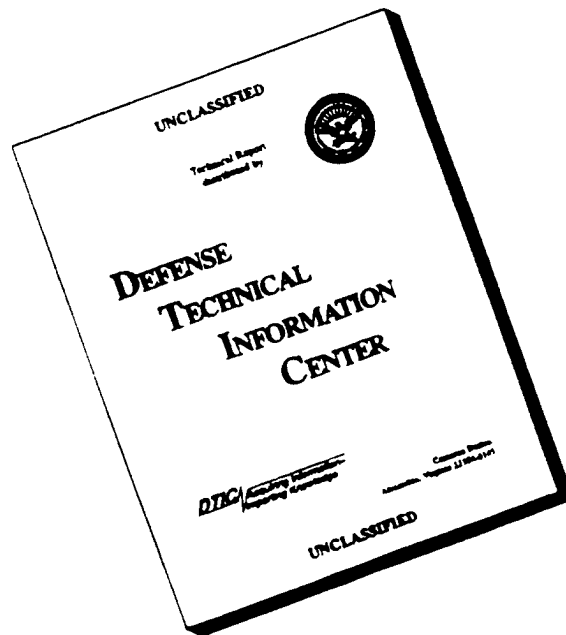
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## ABSTRACT

This report describes work carried out in the Materials Research Laboratory of the Pennsylvania State University over the period August 1, 1993 to July 31, 1993, to evaluate ferroelectric materials in thin film form for power plane decoupling capacitors at very high frequencies. These studies have focused upon compositions in the lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT), lead magnesium niobate:lead titanate (PMN:PT) and lead stannate zirconate titanate (PSnZT). The compositions were carefully chosen to represent ferroelectric, relaxor ferroelectric and antiferroelectric to ferroelectric switching systems which could exhibit ultra high permittivity under the high bias field of the thin film configuration. Results show that the  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  has excellent properties to beyond 20 Ghz. At the switching field PSnZT compositions were demonstrated which have effective capacitance densities of order 1 farad/cm<sup>3</sup>, and permit exploitation of the high spontaneous polarization (40μc/cm<sup>2</sup>) in this system for energy storage purposes.

## DESCRIPTION OF PROJECT

The constantly increasing speed (system clock rate) and steadily increasing density and sophistication of high performance digital circuitry puts sharply increased demands on all components in microelectronic packaging. In particular the speed and the increased number of simultaneous switching events put very heavy demands on the power distribution system. Inductance of the supply and associated distribution lines is generally too large to supply the necessary "instantaneous" currents and high local capacitance is needed to avoid disturbing switching noise. This noise problem becomes particularly troublesome in mixed mode packaging where the noise margin in analogue sections may be orders of magnitude lower. A most satisfactory way to deal with the problem would be an ultra high permittivity single sheet thin film capacitor which could be inserted between power and ground planes as an integral part of the package. Elimination of leads and connections would greatly reduce parasitic inductance providing an effective AC short circuit for high frequency noise. Clearly however an essential need in the ultra high permittivity dielectric is dispersion free operation up to GHz frequencies.

This project aims to investigate the application of ferroelectric thin films as decoupling capacitors in high frequency multichip module (MCM) packages which are operating beyond 1 GHz clock rate. To make full use of the enhanced breakdown strength of these thin film dielectrics, it is essential to operate at high field levels; however, positive dielectric saturation in the conventional ferroelectrics markedly lowers the useful permittivity at high field levels. To modify and improve this deficiency, interest is moving from simple proper ferroelectrics to relaxor ferroelectric (spin-glass) compositions and to antiferroelectric phase switching solid solutions which can generate ultra-high effective capacitance under bias. This study is a collaborative effort of three institutions: Penn State/MRL, Mayo Foundation/SPPDG, and MIT/Lincoln Lab. Penn State is fabricating the thin ferroelectric films, Mayo Foundation

designing the characterization methods, and Lincoln Laboratory fabricating the electrode test structure.

## PROJECT ACCOMPLISHMENTS

Over the last two years, Penn State/MRL has worked on fabricating high-quality pinhole-free ferroelectric thin films, with compositions encompassing simple proper ferroelectric, relaxor ferroelectric, and phase-switching antiferroelectric families, through sol-gel spin-on techniques. The progress to date is summarized as follows:

### *Normal (or Simple, Proper) Ferroelectrics:*

Thin film lead zirconate titanate (PZT) ferroelectrics with compositions in the neighborhood of the morphotropic phase boundary composition  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  are fabricated on platinized silicon wafers. The high frequency dielectric behaviors of PZT thin films are evaluated on a coplanar waveguide test structure with a Hewlett Packard HP8510C vector network analyzer. The preliminary results are shown in Appendix I. Associated properties of these thin-film PZT materials are also reported in Appendix II.

### *Relaxor Ferroelectrics:*

In the relaxor type of ferroelectric compounds such as  $(1-x)\cdot\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\cdot(\text{PbTiO}_3)$ , where  $0 \leq x \leq 1$ , the partially ordered Mg:Nb arrangement on the B site of the  $\text{ABO}_3$  perovskite-type structure leads to ferroelectric spin-glass structures with exceedingly high dielectric permittivity. The PMN:PT(90/10) thin films of 0.5  $\mu\text{m}$  thickness are observed with dielectric permittivity of 1100 and  $\tan \delta$  of 0.01 at a bias of 140 kV/cm.

### *Antiferroelectric:Ferroelectric Phase-Switching Systems:*

Thin film compositions close to the rhombohedral end of the PZT solid-solution phase diagram, which is antiferroelectric (AFE), can be phase switched to ferroelectric (FE) state under strong electrical fields. For these compositions, the forward-switching (AFE  $\rightarrow$  FE) field and the backward-switching (FE  $\rightarrow$  AFE) field can be controlled by composition manipulation. In our study, compositions of the Niobium-doped lead zirconate stannate titanate (PSnZT) show "square" loop hysteresis behavior in low tin, low titanate orthorhombic composition with a maximum polarization of  $40\mu\text{C}/\text{cm}^2$ , and switching fields of 175 kV/cm and 75 kV/cm for the forward and backward switching respectively. The details regarding to the fabrication and properties' characterizations can be referred to Appendix III. The slope permittivity in either switch forward or switch back modes is far higher than available in other systems, leading to effective capacitance of order  $35\text{ }\mu\text{farads}/\text{cm}^2$  or a capacitance density of  $1\text{ farad}/\text{cm}^3$ . A comprehensive summary of these three typical ferroelectric families of thin films is released in Appendix IV.

### **FUTURE APPROACH**

As a future plan, Penn State/MRL will identify and synthesize sol-gel formulations primarily in the lead lanthanum zirconate titanate (PLZT) solid solution system that exhibit normal, anhysteretic, and phase switching characteristics. Films will be fabricated on silicon wafers with platinum diffusion barriers, and tested for their dielectric and ferroelectric properties before extension to sapphire wafers.

In normal ferroelectric thin films, compositions that are of interest include 5/55/45, 7/65/35, and 15/40/60 (La/Zr/Ti). The compositions of non-linear dielectric thin films in PLZT family encompasses 9/65/35, 12/55/45, and 10/55/45 (La/Zr/Ti), which show diffuse phase

transition and relaxor characteristics. Regarding to the phase switchable antiferroelectrics, the compositions that are of interest and will be fabricated on sapphire test wafers include 2/95/5 and 10/75/25 (La/Zr/Ti). In addition, lead hafnate ( $\text{PbHfO}_3$ ) which is isostructural with lead zirconate, and potentially showing high polarization charge at the phase switching field, will be fabricated as thin films.

The above three typical ferroelectric materials and another interesting paraelectric compositions, such as 10.65.35 and 24.10.90 (La/Zr/Ti), will be fabricated as thin films of approximately  $0.5 \mu\text{m}$  thickness on sapphire wafers with coplanar waveguide test structures. The dielectric measurements at high frequency of giga-hertz range will be performed in Mayo Foundation. Penn State and Mayo Foundation will work jointly to analyze experimental data and strategize additional action plans based upon results of analysis.

## **APPENDIX I**



## HIGH FREQUENCY DIELECTRIC PROPERTIES OF THIN-FILM PZT CAPACITORS

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Abstract We present a method for calculating the dielectric constant and the dissipation factor for thin-film ferroelectric capacitors from scattering parameter measurements at multi-gigahertz frequencies. Physical measurement is discussed along with description of the model upon which the calculation is based. Experimental results for 0.5 micron films of PZT are reported up to 15 GHz. Direct measurement is compared with indirectly calculated values at the 100 MHz to 1.5 GHz range, showing excellent agreement.

### INTRODUCTION

The Multichip Module (MCM) offers many advantages for ultra high speed electronics systems. In order to take maximum advantage of MCM technology, it is necessary to confront the fact that current switching transients generated by the integrated circuits (chips) cause rapid voltage fluctuations, or "noise", on the power and ground planes of the MCM. These local and global fluctuations in voltage on the ground and power busses can be so severe that the digital logic, which depends for its voltage references on the DC values of the power and ground busses, can no longer distinguish a logic low signal from a logic high signal.

The traditional solution to this problem has been to employ discrete decoupling capacitors around each chip on the MCM. Another approach is simply to deposit a layer of high-dielectric material as a physical separator between the power and ground planes [1]. In either case, it is clear that materials with high dielectric constants would be desirable, since they would reduce the necessary area and volume dedicated to the decoupling capacitors. Furthermore, the ability to integrate decoupling capacitors to the greatest extent possible will dramatically affect the high

frequency limits of a given MCM technology.[2] Recently, thin-film ferroelectric capacitors have been explored as a solution to this technical challenge. [3,4]

We describe here a method for characterizing materials which might be considered for such applications. We report here only on thin film PZT, but the technique is general and can be applied to any high-dielectric ceramic that exhibits a ferroelectric, non-ferroelectric, or relaxor-ferroelectric behavior.

### SAMPLE PREPARATION

Lead zirconate titanate thin films with Zr/Ti molar ratios of 30/70, 52/48 and 70/30 represented tetragonal, morphotropic phase boundary and rhombohedral compositions; the films were fabricated by the sol-gel spin-on technique. The preparation of the sol was based on a procedure reported earlier [5,6]. Lead acetate trihydrate was dissolved in 2-methoxyethanol in a three neck reaction flask, and refluxed under heat. To remove the water of hydration, refluxing was continued until the temperature of the vapors condensing in the still head reached that of the pure solvent. The dehydrated solution was cooled to room temperature. Titanium isopropoxide and zirconium n-propoxide were then added (inside a glove box) to levels which correspond to the targeted stoichiometry of the films. The resulting solution was refluxed for a few hours, and the byproducts volatalized at 125°C. The final concentration of the solution was adjusted by either the removal or addition of the solvent.

Thin films of the required thickness were obtained by a multi-step spin-on procedure, with intermediate pyrolysis at each step at 400°C. The films were annealed at 700°C for 30 minutes for crystallization. Typically, films thicker than 0.5 micron were fabricated, since an earlier study [7] revealed a thickness dependence of the dielectric and ferroelectric properties of the PZT films for thicknesses less than 350 nm. Phase identification and microstructural investigations were carried out with a Scintag Diffractometer and Scanning Electron Microscope, respectively.

The ferroelectric films were formed on polished single crystal sapphire substrates which were previously patterned with a 200 nm thick evaporated platinum film. In addition to the platinum there was a 40 nm titanium adhesion layer between the platinum and the sapphire substrate. The platinum provides the best available back contact metal to the capacitors because it has minimal interaction with the ferroelectric film during anneal. Sapphire was chosen as the substrate because it also will have minimal interaction with the ferroelectric film.

After deposition, the ferroelectric was removed everywhere except in the areas where the capacitors are to be formed using a photoresist mask and an etch composed of buffered HF, HCl and H<sub>2</sub>O [8]. Using a photo resist lift off process, the top titanium-gold layer is formed which provides the front contact for the capacitors and also completes the coplanar waveguide test structure. The gold is evaporated to a thickness of 0.5 microns which allows a good contact to be made with the coplanar probes used in the measurement.

## EXPERIMENTAL TECHNIQUE

Measurements were performed on parallel plate capacitors mounted in microwave compatible test fixtures. The cross section and plan view structure of the capacitors is diagrammed in Figure 1. Several different sizes of capacitors with varying aspect ratios were fabricated to detect fringing effects or other geometry dependent phenomena. Parasitic inductances in the coplanar waveguides caused the structures to resonate, and for the larger capacitors these resonances led to highly inaccurate results at frequencies above several hundred MHz. However, the smallest capacitors measured 10 microns x 10 microns and yielded accurate results up to 10-15 GHz for the samples studied.

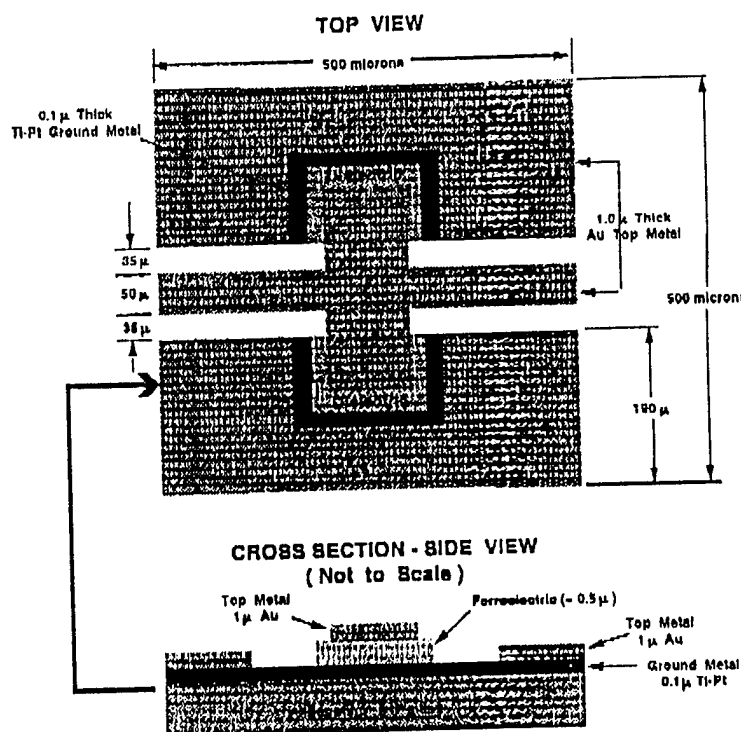


FIGURE 1. Thin film capacitor test structure. (11724)

The electrical properties of several thin film samples were investigated over a frequency range of 300 kHz to more than 10 GHz. To accomplish this measurement over such a broad frequency range, several different instruments were employed. At lower frequencies the capacitance and dissipation factor were directly obtained from two instruments. The HP 4285A LCR meter was used from 300 KHz to 1 MHz, and the HP4291A RF impedance analyzer was used from 1 MHz to 1.8 GHz. At high frequencies the capacitance and dissipation were computed from scattering matrix data. The scattering parameters were measured with an HP 4396 network analyzer from 10 MHz to 1.8 GHz, and with an HP 8510C vector network analyzer

from 100 MHz to 26.5 GHz. We were unable to record accurate data beyond 10-15 GHz because the test structures began to approach their inherent resonant frequencies.

### MODEL

The structures can be modeled by the equivalent circuit shown schematically in Figure 2a. The impedance of the structure, in the form of a T-section, is defined in Figure 2b. We assume that the resistivity of the dielectric material is quite high compared to the capacitive reactance. Therefore we can simplify the impedance  $Z_3$  as

$$Z_3 = \frac{1}{1/R + j\omega C}$$

$$\approx -\frac{j}{\omega C}$$

where

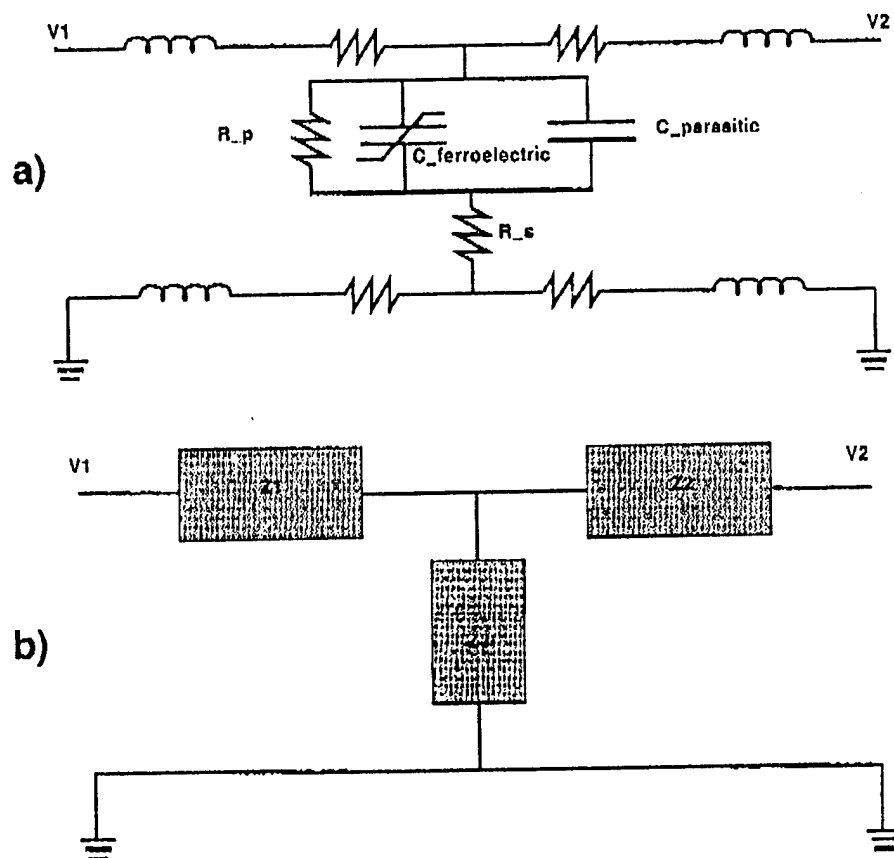


FIGURE 2. a) Circuit model of capacitor test structure; b) equivalent impedances of circuit model (13033)

$$C = C_{\text{ferroelectric}} + C_{\text{parasitic}}$$

We can obtain the capacitance value of the parallel plate ferroelectric capacitors by calculations based on measured scattering parameter measurements. Scattering parameters are defined by the matrix equation

$$\begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \begin{bmatrix} V_1^+ \\ V_2^+ \end{bmatrix} = \begin{bmatrix} V_1^- \\ V_2^- \end{bmatrix}$$

Here the superscript "-" refers to the wave emerging from the test port and the superscript "+" refers to the wave being injected into the test port. We could also describe the circuit in terms of a "transmission matrix" which relates current and voltage at each port and is defined by the matrix equation

$$\begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} \begin{bmatrix} V_2 \\ I_2 \end{bmatrix} = \begin{bmatrix} V_1 \\ I_1 \end{bmatrix}$$

The elements of the transmission matrix and the scattering matrix are then related by a set of linear transformations: It can be shown that [9]

$$T_{21} = \frac{1}{Z_0} \frac{(1 - S_{11})(1 - S_{22}) - S_{12}S_{21}}{2S_{21}} = \frac{1}{Z_3}$$

The impedance  $Z_3$  is in fact merely  $1/T_{21}$ , so once we have computed the T-matrix, obtaining  $Z_3$  is straightforward. From the complex impedance we calculate the total capacitance and the series resistance.

$$R_s = \text{Re}(Z_3)$$

$$C = \frac{-1}{\omega \text{Im}(Z_3)}$$

We subtract the parasitic capacitance (which is typically less than 1% of the total capacitance) to find the capacitance of the ferroelectric capacitors. We then calculate the dielectric constant to be

$$\epsilon_r = \frac{C \cdot d}{A \cdot \epsilon_0}$$

Dielectric loss is given in terms of the dissipation factor, i.e., the inverse of the quality factor. For the capacitors described here, the dissipation factor is

$$D = R_g \omega C$$

## EXPERIMENTAL RESULTS

Our results demonstrate that the three samples all exhibit a decrease in dielectric response with increasing frequency. For the morphotropic and rhombohedral phases, a sharp rolloff in dielectric constant occurs at approximately 1.3 GHz. When the rolloff frequency is reached, the dielectric constant drops by 10-15%. The rolloff is attributed to the frequency of the alternating electric field exceeding the speed of domain wall movement. In other words, the hysteretic polarization of the unit cells no longer contributes to the total polarization,  $P(E)$ , at approximately 1.3 GHz.

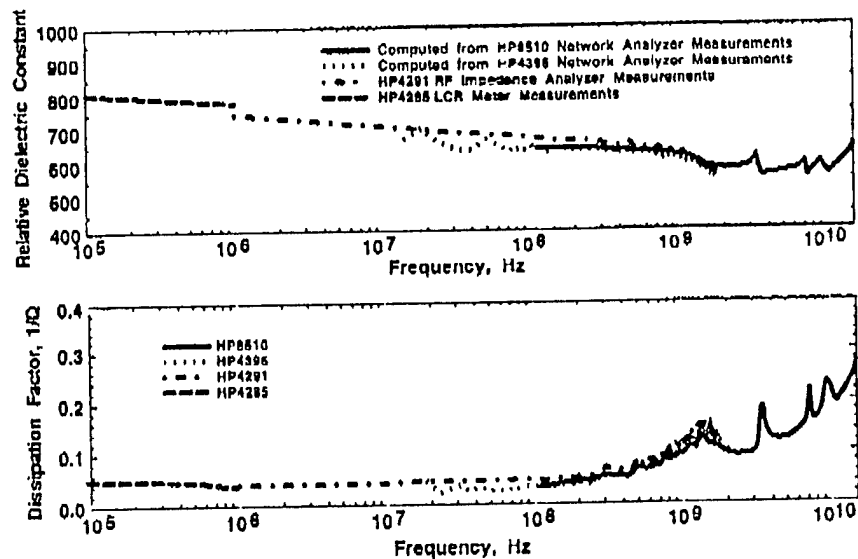


FIGURE 3. Frequency dependent electrical properties of 100 sq. micron PZT(52/48) capacitor, film thickness of 0.5 microns. (12976)

All three compositions of PZT studied exhibit a frequency independent behavior of dielectric constant at frequencies above approximately 1 GHz. Therefore there is an almost linear increase in the dissipation factor of the parallel plate capacitors with respect to frequency. A typical set of measurements over the entire frequency range of this study is presented in Figure 3 for 0.5 micron thick PZT(52/48). A comparison of each composition is shown for the range of 1-10 GHz in Figure 4. Each of the samples were measured at three separate bias voltages. All of the test instruments applied small signal analysis near these bias voltages. The effects of

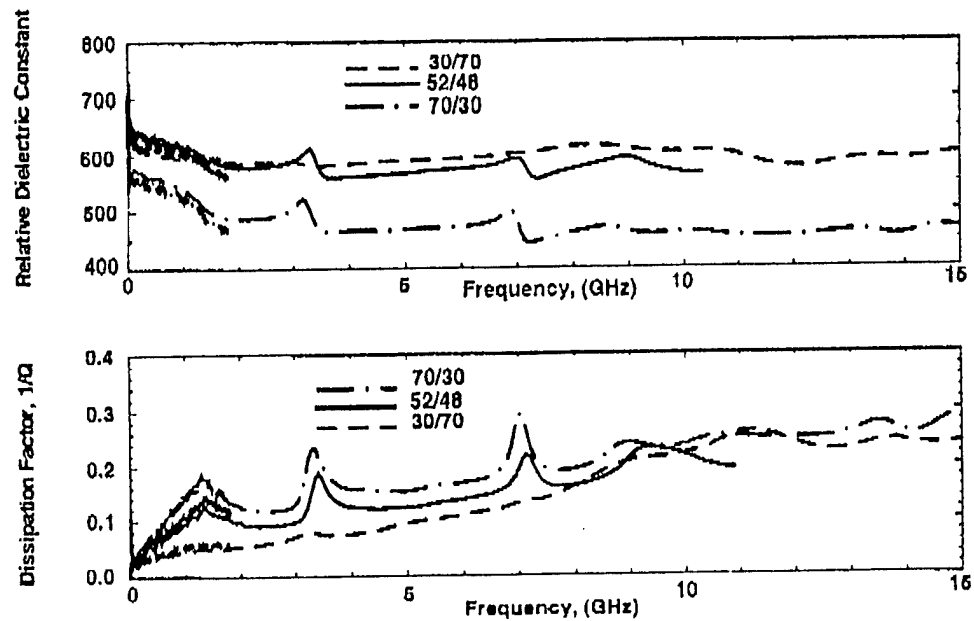


Figure 4. Comparison of high frequency electrical properties of three compositions of 0.5 micron thick PZT dielectric film. (13034)

TABLE 1. DC Bias Dependence of Dielectric Properties of 0.5 micron Thin-Film PZT at 5 GHz.

Composition	Property	Value at:	0V	3V	5V
(52/48)	$\epsilon_r$		550	450	370
	D		0.14	0.125	0.11
(30/70)	$\epsilon_r$		600	580	520
	D		0.09	0.09	0.09
(70/30)	$\epsilon_r$		465	370	300
	D		0.15	0.12	0.10

bias at 5 GHz on the material's dielectric constant and dissipation factor are depicted in Table 1.

### CONCLUSIONS:

We have presented an experimental method which allows the determination of the electrical properties of thin-film dielectrics at multi-GHz frequencies. The method of calculating dielectric constant and dissipation factor yield results which agree extremely well with measurement up to 1.8 GHz, the limit of our direct

measurement capability. We have also demonstrated that the frequency range over which accurate measurements can be obtained can quite likely be extended by fabricating capacitors smaller than the pair of parallel 100 square micron capacitors which provided the best results for the present experiments.

We have also demonstrated that the thin-film, sol-gel PZT retains a very high dielectric constant (about 500) at up to 15 GHz. The dissipation factor increases linearly with frequency over the 1-15 GHz range, achieving values as large as 0.25 for some samples.

#### ACKNOWLEDGEMENTS

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## **APPENDIX II**

## ELECTRICAL PROPERTIES' MAXIMA IN THIN FILMS OF THE LEAD ZIRCONATE-LEAD TITANATE SOLID SOLUTION SYSTEM

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### ABSTRACT

The piezoelectric strain coefficients have been measured as a function of composition for films in the  $\text{PbZrO}_3\text{-PbTiO}_3$  (PZT) solid solution system, using a double-beam laser interferometry technique. This compositional dependence of piezoelectric, and the associated dielectric and ferroelectric properties for films one micron in thickness with varying Zr/Ti ratio, deposited on platinized silicon substrates using a modified sol-gel route, corresponds to data reported for undoped PZT ceramics with respect to the effective morphotropic phase boundary composition. Films with composition near the morphotropic phase boundary,  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ , show enhanced values of the longitudinal piezoelectric coefficient, 194 pC/N; dielectric permittivity, 1310; and remanent polarization, 36  $\mu\text{C}/\text{cm}^2$ .

The compositional dependence of the structure and electrical properties of PZT bulk ceramics has been investigated extensively. Near the composition  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ , ferroelectric phases of tetragonal and rhombohedral modifications co-exist metastably along a boundary which is a strong function of composition, but only a weak function of temperature, known as the morphotropic phase boundary, or MPB. Jaffe et al.<sup>1,2</sup> and Berlincourt et al.<sup>3</sup> have reported enhancements of the dielectric constant and induced piezoelectric effect in compositions near the MPB region. Carl and Härdtl<sup>4</sup> further observed that the maximum in the electromechanical activity is, in fact, caused by the maximum in the dielectric permittivity near the phase boundary composition,  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ ; however, the increased poling efficiency due to the metastable coexistence of tetragonal and rhombohedral phases is also an important factor. PZT ceramic compositions near the MPB have been exploited in many transducer applications for their high electromechanical coupling efficiency.

While conventionally processed ceramics are not amenable to integration with micro-sized transduction devices, films of complex oxide materials, such as PZT, can be readily integrated into silicon device fabrication procedures through a number of deposition techniques, both chemical and physical. The feasibility of using a thin, chemically prepared PZT film as a piezoelectric transduction element in a silicon-based ultrasonic micromotor has been demonstrated by Flynn et al.<sup>5</sup> and Udayakumar et al.<sup>6</sup>, in which it was assumed that the MPB composition is not shifted due to either scaling effects imposed by the sub-micron thickness and grain size or the stress boundary conditions imposed on the film by the relatively massive silicon substrate. As the large electromechanical activity of the PZT compositions would be

expected to couple a change in mechanical state to an electronic reconfiguration, it is not immediately obvious that this assumption is valid, and in this regard several groups have investigated the effect of the Zr/Ti ratio on the dielectric and ferroelectric properties of PZT thin films in the last few years<sup>7-17</sup>, though, perhaps due to the extreme sensitivity of film properties to even subtle variations in processing conditions, no consensus has been reached with respect to the MPB composition. A major lacuna has been the virtual nonavailability of any data on piezoelectric properties as a function of composition. The investigation at hand is intent on elucidating the relationship between the Zr/Ti ratio and the effective longitudinal piezoelectric coefficients of PZT films, and, in a more general sense, further clarifying the relationship between the structure and properties of PZT films.

In this study, a number of  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  compositions, with  $x$  ranging from 0 to 0.8 were prepared by a sol-gel technique similar to that used by Yi et al.<sup>18</sup>. Lead acetate trihydrate was initially dissolved in acetic acid, and the water of hydrolysis was expelled during a brief distillation at 105°C. Zirconium and titanium alkoxides were then added in the proportions dictated by the composition; excess lead, 10% by mole, was added to solutions throughout to compensate for lead loss during firing and to stabilize the perovskite phase. Ethylene glycol and water have been added to the final solution to adjust the viscosity and surface tension, reducing the likelihood of cracking during pyrolysis. The resulting solution, stable in air and relatively concentrated with a molarity of 0.9, is used to fabricate films through a multilayer spin-on procedure. After deposition on to (100) silicon wafers with a 0.15  $\mu\text{m}$ -thick platinum electrode sputtered on a 0.5  $\mu\text{m}$ -thick thermally grown  $\text{SiO}_2$  buffer and a 0.02  $\mu\text{m}$ -thick Ti adhesion layer, each layer was dried at 150°C and

pyrolyzed at 550°C to preclude the entrapment of organics by subsequent layers. After four depositions in this manner, the multilayer structures were annealed at 700°C for one hour, resulting in perovskite films 1  $\mu\text{m}$  in thickness. To facilitate electrical property measurements, platinum top electrodes of 0.8 and 1.6 mm diameter were sputter-deposited.

Whereas in the case of bulk ceramics, sample quality can be evaluated by routine, quantitative determinations of density and weight loss, film quality is more commonly determined from the microstructure in electron micrographs. The scanning electron micrographs of the surface and cross-section of a representative PZT(52/48) film are presented in Fig. 1, from which a dense, layered structure with a bi-modal grain distribution is revealed, indicating, in concert with X-ray diffractograms, the predominance of single phase, high quality film volume.

Following initial poling under 150 kV/cm dc field for 2 minutes at room temperature, each sample was characterized for field-induced strain in a highly-sensitive double beam laser interferometer<sup>19</sup> by applying varying dc bias over a fixed, 1 kHz ac field of 1 kV/cm (rms value). The effective longitudinal piezoelectric coefficient,  $d_{33}$ , is calculated from the converse piezoelectric effect. The effect on  $d_{33}$  of a positive, increasing external dc bias is shown in Fig. 2 for a  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  composition, from which a maximum effective  $d_{33}$  of 194 pC/N is discerned, at an external bias field of 40 kV/cm. The reduction of  $d_{33}$  beyond a certain external bias value is due to the effective restraint of domain wall movement, and hence the loss of significant extrinsic contributions.

It is important to establish that the definition herein of the "effective"  $d_{33}$ , plotted in Fig. 3 as a function of composition, is the maximum value of  $d_{33}$  observed as an increasing dc bias is imposed over a fixed ac driving field. The composition of maximum effective piezoelectric coefficient, ( $d_{33} = 194$  pC/N), perhaps referred to as the effective morphotropic phase boundary composition, and consequently the composition of highest electromechanical activity and transduction efficiency, contains 48%  $\text{PbTiO}_3$  in solid solution, identical to the reported ceramic composition. Comparison between observed  $d_{33}$  values for PZT films and that of the bulk ceramics<sup>3</sup> shows similar trends, although the peak width of the films is larger and the peak value is lower than that of the bulk ceramics ( $d_{33} = 223$  pC/N). The slightly lower peak value of  $d_{33}$  in PZT films might be attributable to clamping from the stiff substrate and non-optimal room temperature poling to which the films are limited.

While the primary objective of this undertaking, as stated earlier, has been the study of the variation of the piezoelectric properties as a function of composition in the PZT solid solution system, the inherent relationship<sup>6</sup> between the piezoelectric coefficients on the one hand, and the dielectric and ferroelectric properties on the other compels a further examination of the latter properties. The plot of dielectric permittivity as a function of composition for films in the PZT solid solution system suggests the similar occurrence of a morphotropic phase boundary near  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  (Fig. 4). Juxtaposition of this data with bulk ceramic data<sup>3</sup> reveals a fundamental similarity, albeit a narrower peak distribution. Polarization-electric field hysteresis plots for several representative compositions near the MPB, shown in Fig. 5, indicate that the PZT(52/48) film has the largest value of remanent polarization. Compositional distribution of remanent polarization and coercive

field, extracted from P-E traces is plotted in Fig. 6. While no simple relationships can be gleaned from the polarization profile, the maximum remanent polarization of  $36 \mu\text{C}/\text{cm}^2$  is located at 48% of PT in the PZT system. The coercive field, displayed as a function of the mole% of  $\text{PbTiO}_3$ , increases dramatically with the degree of tetragonality.

In summary, compositions in the lead zirconate-lead titanate solid solution system were prepared as films one micron in thickness, deposited by a sol-gel spin-on process on 1" platinized silicon substrates, and characterized with respect to piezoelectric, and the associated dielectric and ferroelectric properties. The position of the morphotropic phase boundary, as determined from significant enhancements in the effective longitudinal piezoelectric coefficient, dielectric permittivity and remanent polarization, coincides with the commonly quoted bulk ceramic composition,  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ . Values of maximum piezoelectric coefficient, 194 pC/N; dielectric permittivity, 1310; and remanent polarization,  $36 \mu\text{C}/\text{cm}^2$ , quoted for the phase boundary composition, compare favorably with values reported for undoped PZT ceramics.

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**FIGURE CAPTIONS**

- Fig. 1 Planar and cross-sectional microstructures of 1  $\mu\text{m}$ -thick PZT(52/48) film.
- Fig. 2 The dc bias dependence of the effective  $d_{33}$  plotted for a 1  $\mu\text{m}$ -thick PZT(52/48) film. The driving field applied corresponds to 1 kV/cm (rms) at 1 kHz. Note that the maximum value is 194 pC/N.
- Fig. 3 The effective  $d_{33}$  as a function of composition in the PZ-PT solid solution system. The experimental points here correspond to the maximum in  $d_{33}$  obtained from plots generated for different compositions; notice that Fig. 2 is one such plot, for the PZT(52/48) composition. The dotted line represents the data reproduced from Berlincourt et al.<sup>3</sup>
- Fig. 4 The dielectric permittivity versus composition in the  $\text{PbZrO}_3$ - $\text{PbTiO}_3$  solid solution system. The top contact electrode is platinum 1.6 mm in diameter. Test signal is 0.1 kV/cm at 1 kHz. The data for bulk ceramics are referenced from Berlincourt et al.<sup>3</sup>
- Fig. 5 A composite trace of ferroelectric P-E hysteresis loops for five neighboring compositions of 1  $\mu\text{m}$ -thick film near the MPB of the PZT system. The top electrode size is 0.8 mm dia. The test signal is a triangular wave with a frequency of 10 Hz.
- Fig. 6 The remanent polarization and coercive field as a function of Zr/Ti ratio in the PZT system. Note that the maximum  $P_R$  is located at the PZT(52/48) composition. Ti-rich compositions show seemingly high coercive fields.

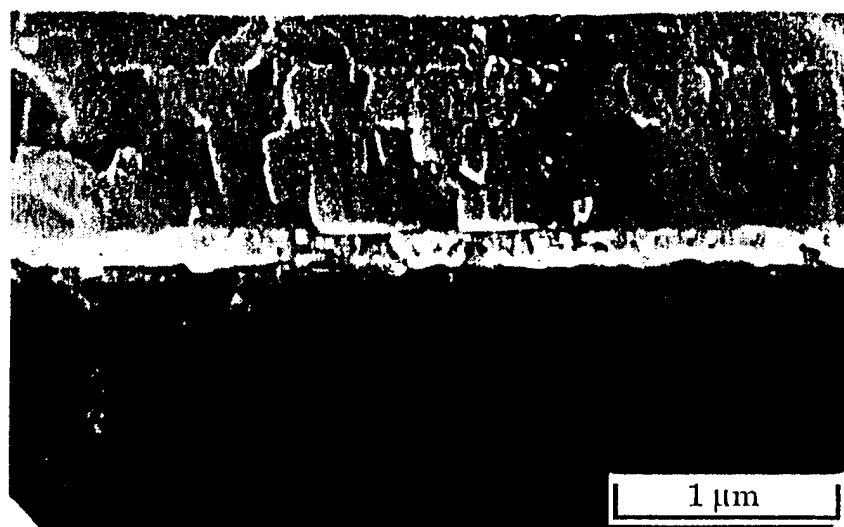
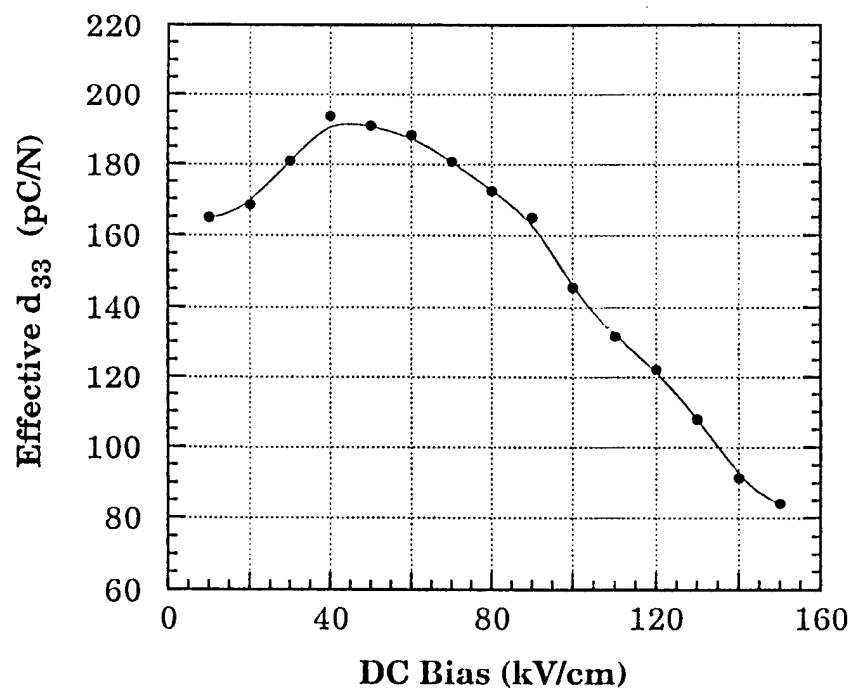


Fig. 1  
Chen et al.



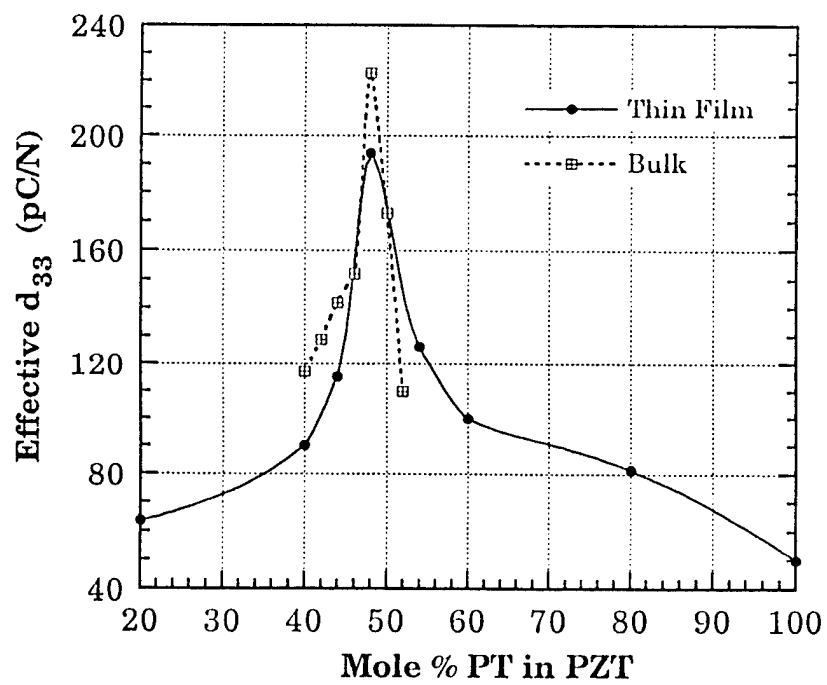
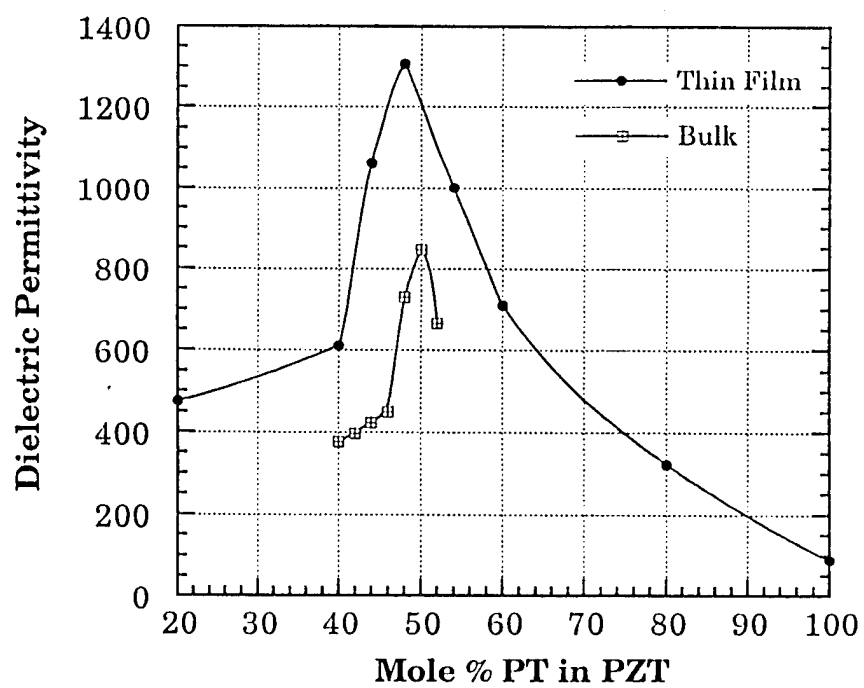


Fig. 3

Effective  $d_{33}$  vs. Mole % PT in PZT



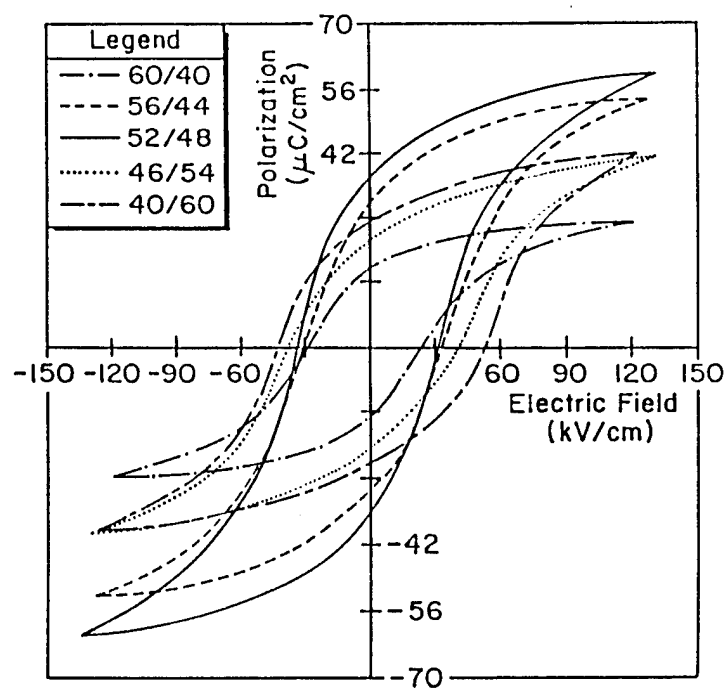


Fig. 5  
Chen et al.

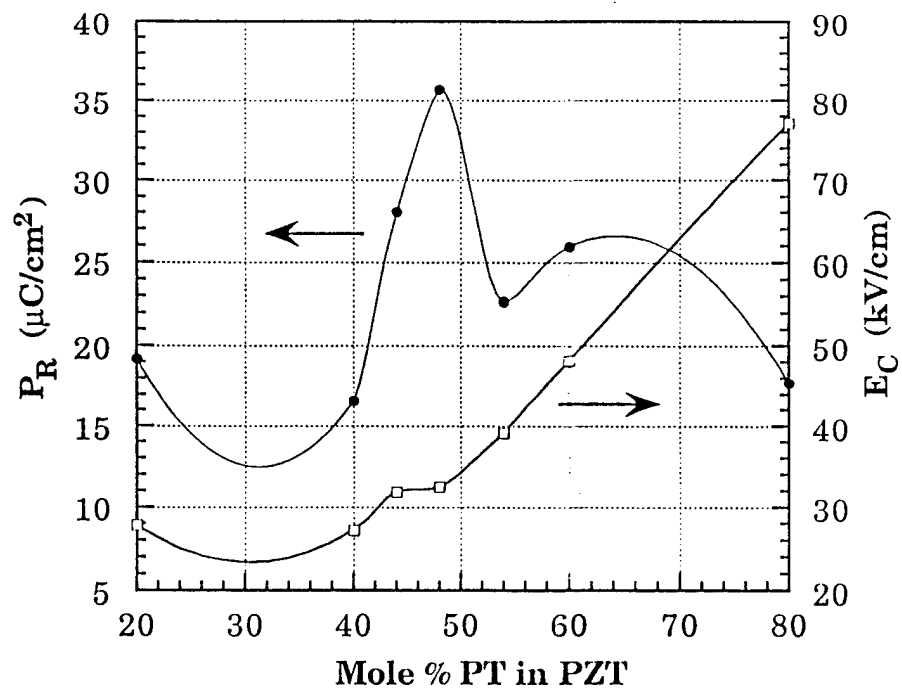


Fig. 6  
chart 1



## **APPENDIX III**

## **"Square" hysteresis loops in phase switching Nb-doped lead zirconate stannate titanate thin films**

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### **Abstract**

Niobium doped lead zirconate stannate titanate thin films have been prepared by a modified sol-gel spin on technique, utilizing the hydrolysis-resistant precursor lead acetylacetonate. Films of compositions in the antiferroelectric tetragonal and antiferroelectric orthorhombic phases were prepared and phase switched with the application of appropriate electric fields. A distinctly "square" hysteresis response was observed in a low titanium, low tin, orthorhombic composition, with a maximum polarization,  $P_{\max}$ , of  $40 \mu\text{C}/\text{cm}^2$  and switching field values of  $E_f = 175 \text{ kV}/\text{cm}$  and  $E_a = 75 \text{ kV}/\text{cm}$ , while varying degrees of squareness, along with lower polarizations and switching fields, were observed in the higher tin, tetragonal compositions. Electric field-induced strains of up to 0.33% have been measured in the orthorhombic composition, with tunable electromechanical coefficients. Film properties showed only slight variation with electrode size over a range of diameters from 0.8 mm to 6.35 mm; large area electrodes are vital for practical actuator and sensor devices. With a capacitance density of 30-35  $\mu\text{F}/\text{cm}^2$ , films of the orthorhombic composition are promising as power plane decoupling capacitors in multi-chip modules.

## I. INTRODUCTION

The electric field forced antiferroelectric (AFE) to ferroelectric (FE) phase transition in ceramic  $\text{PbZrO}_3$  was first demonstrated within a narrow region below its Néel temperature by Shirane et al.<sup>1</sup> Through a series of isovalent and A-site vacancy substitutions, Jaffe<sup>2</sup> and Berlincourt et al.<sup>3,4</sup> were able to broaden the phase-switchable temperature region, allowing for a number of practical applications of these electric field, pressure and temperature switchable antiferroelectric ceramics. Because of the small free energy difference between the AFE and FE phases, switching from one phase to another is possible by the application of a reasonable electric field. Jaffe coined the term "soft" to describe an antiferroelectric which can be field-switched.<sup>2</sup>

Soft antiferroelectrics were proposed as high-energy-storage capacitors by Jaffe because they are free of remanence, like a linear capacitor, and also because the "energy area" traced out by the P-E hysteresis loop approaches a square rather than a triangle, as is the case with a linear element. When the poled FE phase is switched to the AFE phase, the polarization charge is released supplying high currents.<sup>2</sup> Soft antiferroelectrics have also been investigated as transducer materials due to the large strains concurrent with AFE to FE switching. Strains of 0.1-0.5%, depending on the composition, result from transitions between the AFE tetragonal and FE rhombohedral phases, due to specific volume differences. Transitions can be forced by temperature and pressure, as well as

applied electric field, making these materials useful as pressure and temperature transducers.<sup>3,4</sup>

Berlincourt<sup>4</sup>, in a study of doped  $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$  ceramics, has described two different types of AFE-FE transitions based on the character of the P-E hysteresis loops; the two types of loops have been termed "slanted" and "square". The "slanted" loop materials have much less hysteresis, lower transition fields, smaller volume differences between AFE and FE phases, and wider temperature ranges over which the transition can be forced by electric field. The "slanted" loop materials exhibit a small remanent polarization at zero field, while the "square" loop materials do not. Representative P-E hysteresis traces for slanted and square loop compositions are shown, with indications of switching field nomenclatures, in Fig. 1.

Owing to the dramatic changes in polarization and strain accompanying the AFE-FE transition, these materials have been identified as promising candidates for use as high-energy-storage capacitors and electromechanical transducers. However, even at an early stage in their development, limitations inherent to the bulk ceramic form of these materials, namely low dielectric strength and a practical minimum thickness, were identified as deleterious to their extensive utility.<sup>2</sup> Thin ceramic films offer advantages of high dielectric strength (on the order of 1MV/cm), low voltage operation and the possibility of integration into micro-type device schemes. These advantages are especially useful in the study and application of phase switching systems.

The phase switching behavior of thin films in the La-doped PSZT system has been investigated by Brooks et al.<sup>5,6</sup> A number of compositions in varying proximity to the AFE-FE phase boundaries were prepared using a sol-gel spin coating method and characterized for electrical properties and strain. All of the thin film compositions studied (identical to those of Pan et al.<sup>7</sup> in bulk ceramics) showed remanent, "slanted" hysteresis loops.<sup>5,6</sup> The transition fields for the films were found to be larger than the bulk ceramics, while the maximum polarizations and strains measured in the films were lower. Residual tensile stresses due to substrate clamping and a metastable coexistence of FE and AFE phases were given as possible explanations for the observed remanence and lower strain.<sup>5,6</sup>

While the strains resulting from the field-forced AFE-FE transition make La-doped PSZT films useful for microactuator applications, the "slanted" loop hysteresis behavior is not desirable for the high-energy-storage capacitors mentioned by Jaffe.<sup>2</sup> The motivation for this work was to examine Nb-doped lead zirconate stannate titanate thin films in the hope of finding compositions that show "square" loop switching behavior with low remanence and large strains. In addition to an orthorhombic composition, two AFE tetragonal compositions, similar to a composition studied by Berlincourt et al.<sup>3,4</sup>, were investigated to allow for a comparison of thin film and bulk ceramic properties.

For piezoelectric and phase-switching applications in micromechanical systems, large (several mm<sup>2</sup>) electrode areas are

required. A practical maximum electrode area is dictated by defects in the film, which can cause either shorting or high losses. In this study, lead acetylacetonate, which is less sensitive to hydrolysis, has been used as a precursor in an effort to reduce the number of defects in the films, allowing for the use of larger electrodes.

## II. EXPERIMENTAL PROCEDURE

The method used to prepare the solutions was a variant of the sol-gel procedure proposed by Selvaraj et al.,<sup>8</sup> using lead acetylacetonate as an alternative lead source to the more common lead acetate trihydrate. Other precursors used were titanium isopropoxide, zirconium n-propoxide, tin (IV) acetate, and niobium ethoxide. In a unique, one step process, all of the precursors were initially combined with the solvent 2-methoxyethanol, and the mixture was refluxed at 130°C for approximately 12 hours. The solution was then allowed to cool to room temperature, the volume was adjusted for a 0.4 M concentration, and 4% formamide was added to promote proper drying.<sup>10</sup>

Thin films of the various compositions were prepared using a multiple layer spin coating procedure. Each precursor solution was filtered through a 0.2  $\mu\text{m}$  filter and deposited on a substrate, which was spun at 3000 rpm for approximately 30 seconds on a commercial resist spin-coater. The substrate structure consisted of a 0.5  $\mu\text{m}$ -thick thermally grown  $\text{SiO}_2$  buffer layer on (100) silicon wafers with a 0.15- $\mu\text{m}$ -thick platinum bottom electrode sputtered on

a 200Å titanium adhesion layer.<sup>11</sup> After the application of each layer, the films were pyrolyzed at approximately 400°C for 5 minutes to remove organics and allowed to cool to room temperature. Subsequent layers were applied until a thickness of greater than 0.4 μm was achieved. The films were then furnace annealed at 700°C in air for 15 minutes to achieve crystallization into the perovskite structure.

Platinum top electrodes of diameters ranging from 0.8-6.35 mm were deposited by rf sputtering and then annealed at 550°C for one hour to improve electrical contact. The polarization-electric field (P-E) hysteresis loops were measured using a modified Sawyer-Tower circuit at room temperature. Samples were driven with a 5-20 V, 30 Hz signal. The low field dielectric permittivity and dielectric loss tangent of the films were measured at room temperature using an HP4274A impedance analyzer with an oscillating voltage of 1 mV and a frequency of 1 kHz. Capacitance as a function of slowly varying dc bias field was collected with an HP4192A impedance analyzer. With the oscillating field and frequency set at 10 mV and 100 kHz, respectively, the dc bias was stepped through 0.5 V increments in a cyclic manner between -10 and +10 V. The thickness of the films was determined using a profilometer. The crystal phases were characterized by grazing angle x-ray diffraction, using a Scintag DMC-105 diffractometer. Field induced strains were measured using a double beam laser interferometer which has the capability of measuring displacements to a resolution of  $10^{-2}$  Å.

### III. RESULTS AND DISCUSSION

The thickness of the films ranged from 0.4-0.56  $\mu\text{m}$ , as determined from the profilometer traces. X-ray diffraction patterns taken for films of the three compositions verified the presence of pseudo-cubic, perovskite phase reflections. The room temperature, low field relative dielectric constant,  $\epsilon_r$ , the dielectric loss tangent,  $\tan \delta$ , and the phase switching parameters of the three compositions are shown in Table 1, for an electrode diameter of 2.36 mm. The dielectric constants of the two tetragonal compositions are considerably higher than that of the orthorhombic composition. It was noticed that annealing the top electrode lowered the loss considerably and the dielectric constant slightly.

The P-E hysteresis plot for composition #2 is shown in Figure 2. Both tetragonal compositions, #1 and #2, showed this type of behavior, which can perhaps be described as a cross between the square and slanted types of loops, with slightly slanted transitions, high maximum polarization and near zero remanence. It should be noted that compositions #1 and #2 are very similar to a composition presented by Berlincourt et al.<sup>3</sup> as exemplary of the square loop type behavior, thus indicating a difference in the compositionally determined switching behavior in thin film form, although not as drastic a difference as previously suggested.<sup>5,6</sup> Magnitudes of the polarization and switching fields are similar to values found in Berlincourt.<sup>3</sup>



Figure 3a shows the P-E loop for orthorhombic composition #3, which demonstrates, for the first time, a thin film AFE exhibiting the "square" loop hysteresis. The forward and reverse switching fields are quite distinct, and the polarization is nearly zero at zero applied field, in contrast to the slanted loop phenomenon. Thin films of this antiferroelectric phase switching, orthorhombic composition may be extremely valuable as dielectrics for power and ground plane decoupling in advanced multichip modules (MCMs). In an application where the available top surface area is severely limited and the clock rates are continuously on the rise, there is a need for off-chip capacitors that can generate ultra-high capacitance density. Focussing on the FE  $\rightarrow$  AFE arm of the double hysteresis loop in Fig. 3a, a polarization charge of  $16 \mu\text{C}/\text{cm}^2$  may be released for a small voltage change of 0.5 Volt; this corresponds to a capacitance per unit area of  $32 \mu\text{F}/\text{cm}^2$ , a magnitude larger than the  $1 \mu\text{F}/\text{cm}^2$  requirement projected for decoupling capacitors at microwave frequencies. While this magnitude of capacitance density clearly shows great promise, the dielectric saturation function and the charge delivery speed are being examined at GHz frequencies to ascertain the applicability of the films in MCMs. Experiments are currently underway, involving the manipulation of film processing parameters and synthesis of related formulations in the Nb-doped PSZT ternary, to close the gap between the forward and backward switching arms of the loop so that the entire spontaneous polarization may be used to discharge current at constant voltage; the dielectric would, then, essentially behave as a battery, ideally suited for the decoupling function.

The maximum polarizations and switching fields of the tetragonal compositions are lower than those of the orthorhombic (the switching fields given in Table 1 were determined from the P-E loops). In terms of applied voltages, the AFE-FE switching thresholds correspond to 2.4V, 3.4V, and 7.0V for a 0.4 $\mu$ m film of compositions #1, #2 and #3 respectively. Film thickness can be adjusted to decrease the required switching voltage. It is interesting to note that while compositions in the orthorhombic phase field have not been considered in bulk ceramic studies, as their switching fields exceeded dielectric breakdown strengths, it is these compositions, field-switchable in thin film form, which have been identified herein to exhibit the desired "square" loop behavior at the sub-micron scale.

The square loop behavior of composition #3 is reproduced with a 5.94 mm diameter top electrode (Fig. 3a). Note that the polarization has decreased slightly, while the switching fields remain constant. The same general trend was seen for all three compositions with increasing electrode area: slight decreases in polarization and dielectric permittivity, with no change in the switching fields. This type of deviation would be expected to arise from a random, spatial distribution of defects, possibly in the form of pores and grain boundaries, throughout the volume of the film.<sup>12</sup> The ability to use large area top electrodes facilitates the use of these films in devices involving sensing, actuating, and motor functions.

Plots of capacitance versus dc bias have been used to confirm the antiferroelectricity of thin films exhibiting "slanted" loops<sup>5</sup>; Figure 4 shows capacitance as a function of slowly varying bias field,

taken from a virgin electrode, for composition #3. The presence of the "double butterfly" variation, a general characteristic of a soft antiferroelectric, corresponds to the forward and reverse switching fields of the phase transition. The magnitudes of the switching fields can be determined both from the peaks of the C-V curves, and from the intersections of the tangents drawn to the steepest portions of the P-E curves. The two differently determined values are in good agreement as seen in the values for composition #3; the values of forward and reverse thresholds as determined from the C-V data are 150 and 78 kV/cm, while the corresponding values determined from the P-E curves are 175 and 75 kV/cm, respectively.

The electric field induced longitudinal strain for a film of composition #3 is shown in Fig. 5 as a function of ac drive field at a dc bias of 100 kV/cm. The strain is low at ac fields below 40 kV/cm, but reaches a value of 0.33% at 100 kV/cm. There is no data available in the literature for bulk ceramics of equivalent composition with which this strain data may be compared. A strain of 0.16% for a La-doped film of composition  $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.60}\text{Ti}_{0.10}\text{Sn}_{0.30})\text{O}_3$  has been reported.<sup>5</sup> An effective longitudinal piezoelectric coefficient,  $d_{33}$ , calculated through the converse piezoelectric effect (from the data presented in Fig. 5) is plotted in Fig. 6. It is apparent from the figure that the effective  $d_{33}$  can have a value as large as 250 pC/N, and is tunable with appropriate drive and dc bias conditions.

#### IV. SUMMARY

Sol-gel derived thin films of antiferroelectric to ferroelectric phase switching Nb-doped lead zirconate stannate titanate have been prepared, making use of an alternate lead precursor, lead acetylacetonate. Electric field induced strains of up to 0.3% have been optically determined for an AFE orthorhombic composition, representing the highest value for the phase switching family of antiferroelectrics reported to date. Large area electrodes, up to 6.35 mm in diameter, have been successfully employed. Composition #3 shows a square, double P-E loop, and with a high capacitance density, is promising for applications as a decoupling capacitor in multi-chip modules. The low remanence observed in compositions #1 and 2 suggests that the Nb-doped  $\text{PbZrO}_3$ - $\text{PbSnO}_3$ - $\text{PbTiO}_3$  ternary system provides a family of highly useful compositions, from which desired characteristics can be chosen, for applications as energy storage devices and in micromechanical systems. A closer, more detailed examination of the phase diagram is needed, specifically of the compositions that lie along the boundary of the AFE orthorhombic and FE rhombohedral regions, as the results of composition #3 are very promising.

#### ACKNOWLEDGEMENT

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**Table Caption**

Table I. Summary of dielectric and phase switching characteristics of Nb-doped lead zirconate stannate titanate thin films.

### Figure Captions

Fig. 1 Delineation of slanted and square switching behavior, reproduced from Berlincourt.<sup>4</sup> Also indicated are definitions of forward and backward switching fields,  $E_f$  and  $E_a$ .

Fig. 2 P-E hysteresis trace for AFE tetragonal composition #2.

Fig. 3 "Square" P-E hysteresis behavior as seen in AFE orthorhombic composition #3 for electrode diameters of a). 1.6 mm and b). 5.94 mm, showing little degradation of maximum polarization.

Fig. 4 Plot of capacitance as a function of varying dc bias for a film of AFE orthorhombic composition #3.

Fig. 5 Field induced strain as a function of ac driving field at 1 kHz for composition #3. The film was maintained at a dc electric bias of 100 kV/cm.

Fig. 6 Effective  $d_{33}$  as a function of drive field for composition #3.

Table 1: Summary of phase switching characteristics of Nb-doped lead zirconate stannate titanate thin films

Film Composition	Thick- ness ( $\mu\text{m}$ )	$\epsilon_r$ at 1kHz	$\tan \delta$	$E_{\text{AFE} \rightarrow \text{FE}}$ (kV/cm)	$E_{\text{FE} \rightarrow \text{AFE}}$ (kV/cm)	$P_{\text{max}}$ ( $\mu\text{C}/\text{cm}^2$ )
1) $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.57}\text{Sn}_{0.38}\text{Ti}_{0.05})_{0.98}\text{O}_3$	0.56	530	0.015	60	30	26
2) $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.65}\text{Sn}_{0.31}\text{Ti}_{0.04})_{0.98}\text{O}_3$	0.44	530	0.016	85	45	35
3) $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.85}\text{Sn}_{0.13}\text{Ti}_{0.02})_{0.98}\text{O}_3$	0.45	240	0.005	175	75	40



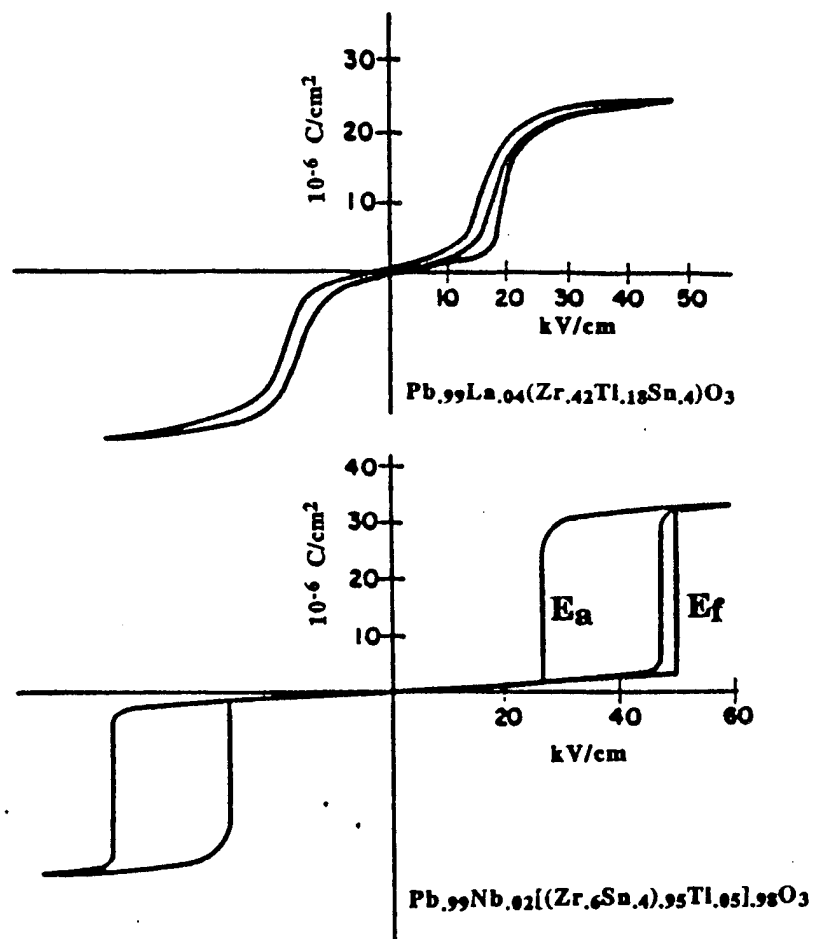


Fig. 1  
Gasky et al.

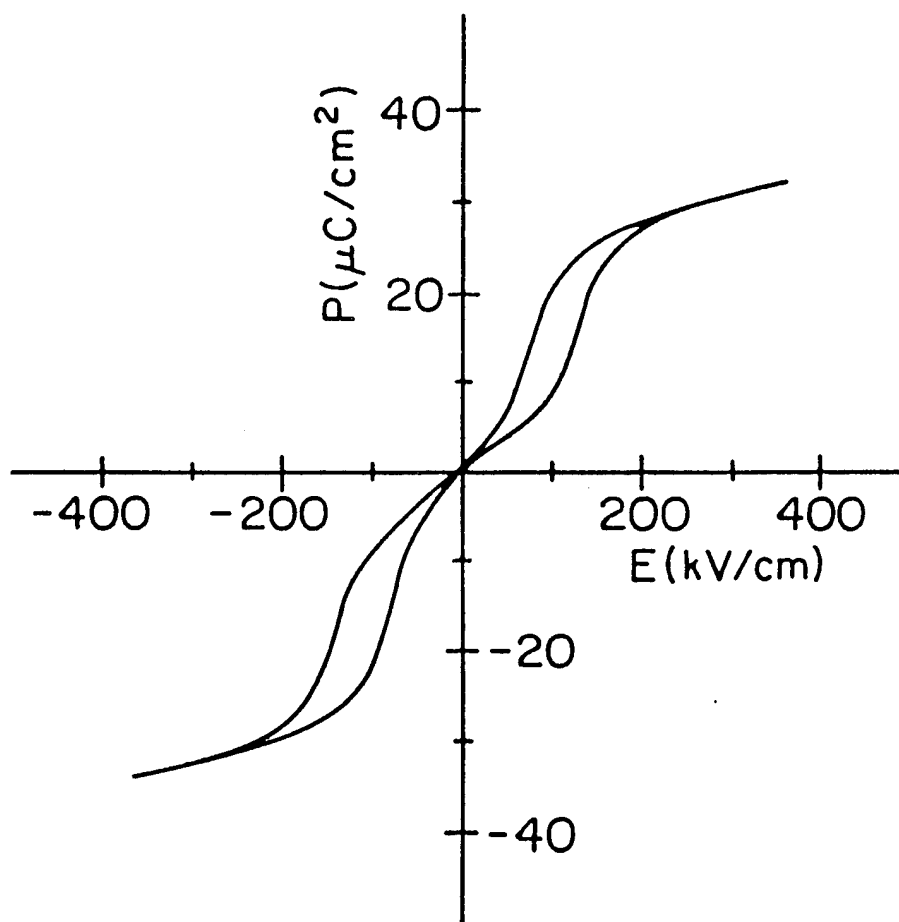


Fig. 2.

Gaskey et al.

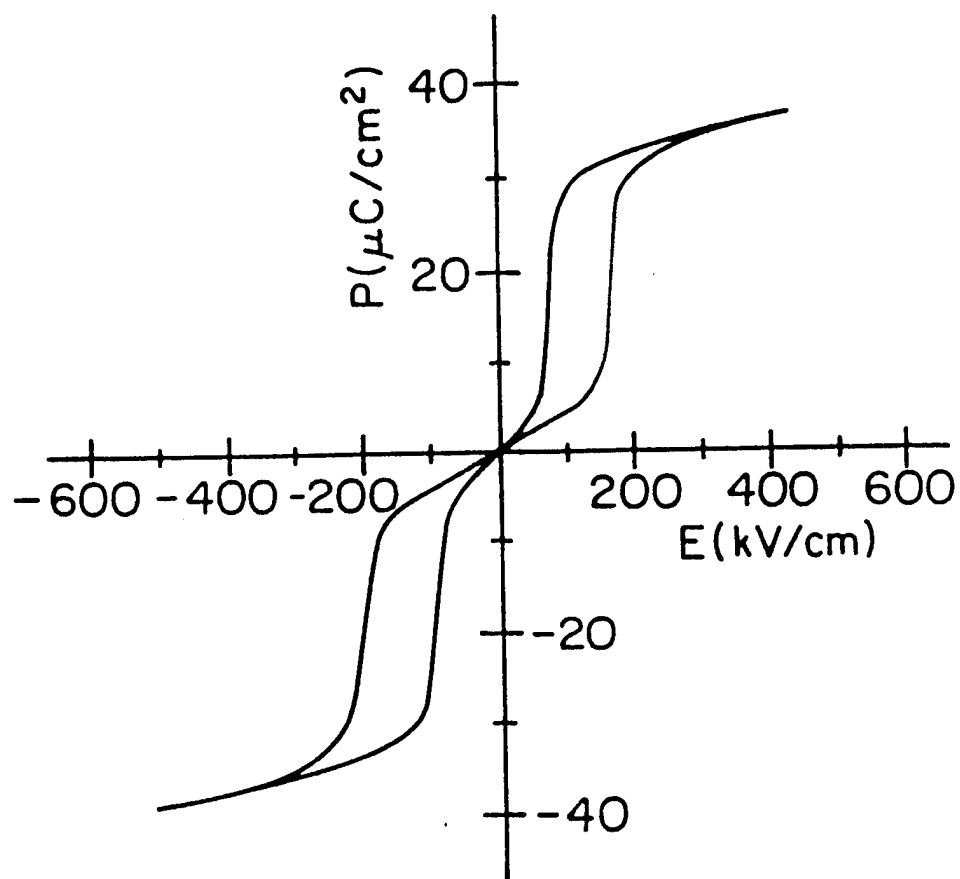


Fig. 3a  
Gaskey et al.

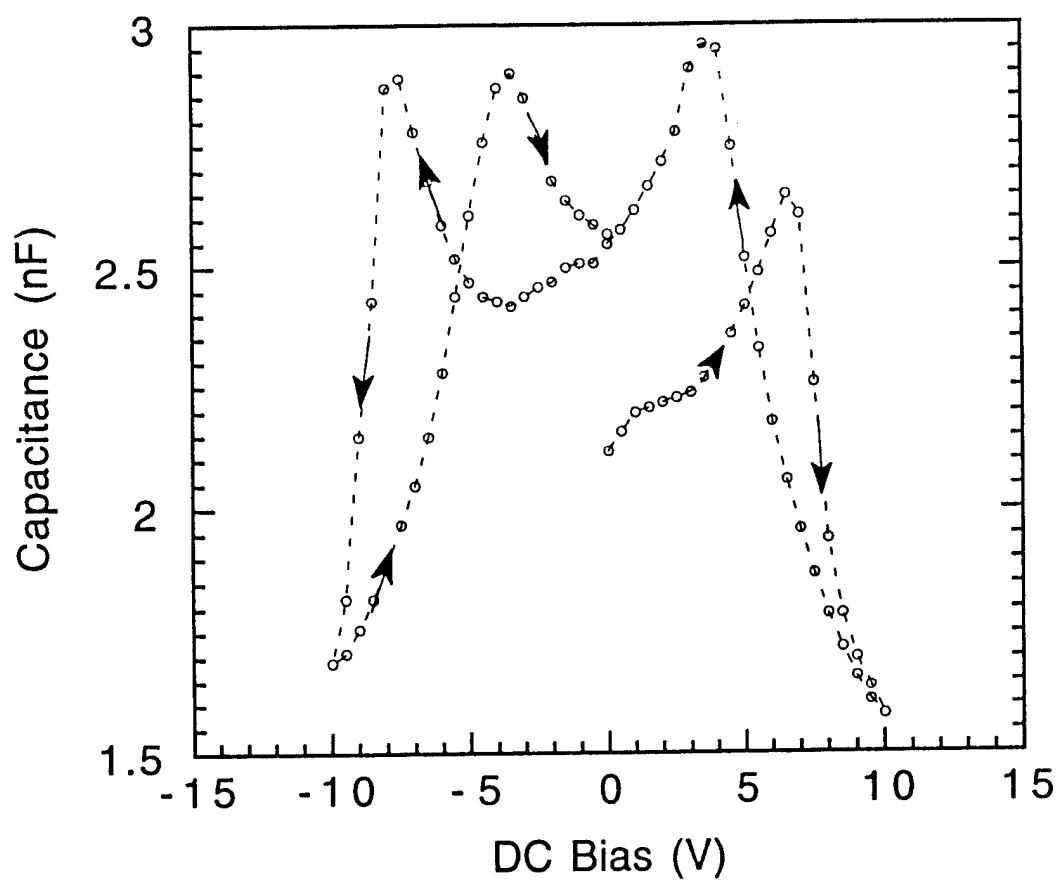


Fig. 4  
Gaskey et al.

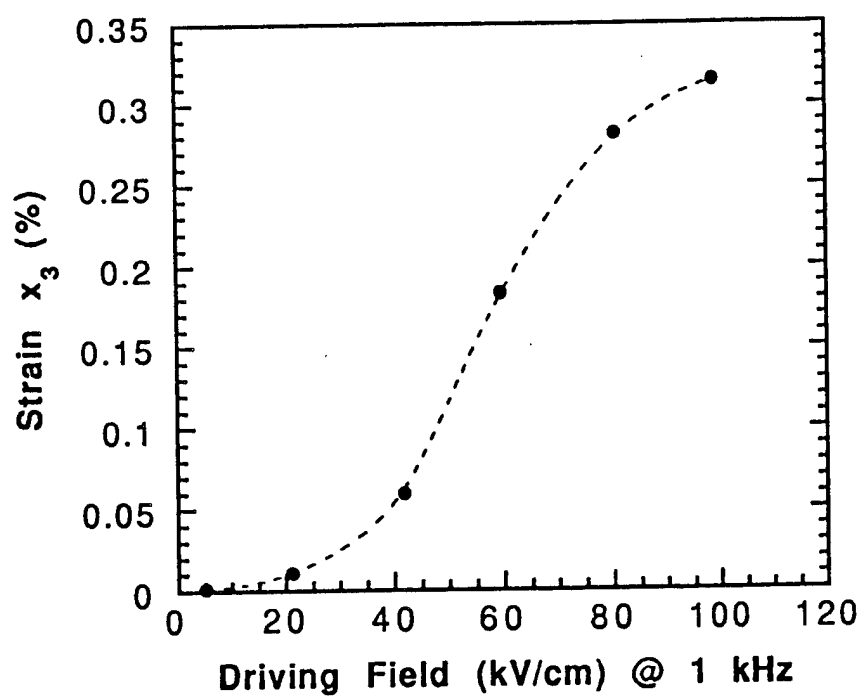


Fig. 5  
Gaskey et al.

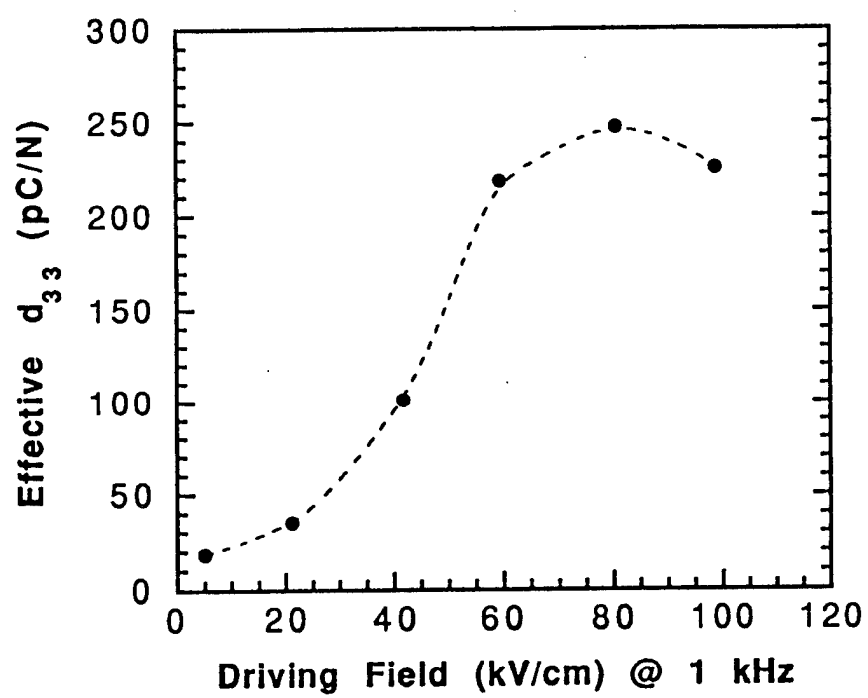


Fig. 6  
Gasky et al.

## **APPENDIX IV**

## EVALUATION OF FERROELECTRIC MATERIALS FOR POWER PLANE DECOUPLING CAPACITORS AT FREQUENCIES ABOVE 1 GHz

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Materials Research Laboratory  
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University Park, PA 16802

This project aims at the investigation of ferroelectric thin films as decoupling capacitors in high frequency multichip module (MCM) technology. To make full use of the enhanced breakdown strength of these thin film dielectrics it is essential to operate at high field levels, however positive dielectric saturation in the conventional ferroelectric markedly lowers the useful permittivity at high field levels. To modify and improve this non linearly interest is moving from simple proper ferroelectrics to relaxor ferroelectric (spin glass) compositions and to antiferroelectric phase switching solid solutions which can generate ultra-high effective capacitance under bias. The study is a collaborative effort of three institutions; Penn State University/MRL, Mayo Foundation SPPDG, and MIT Lincoln Laboratory. Penn State is fabricating the ferroelectric films, Mayo Foundation designing the measuring methods and Lincoln Lab fabricating the electrode test structures.

Progress to date has yielded:

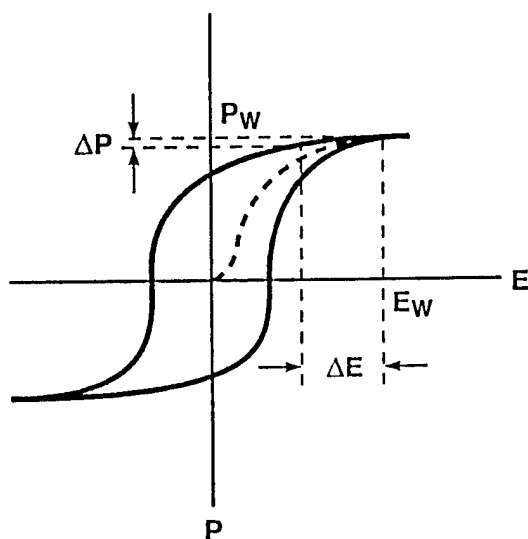
PZT 52/48 with  $\epsilon = 750$   $\tan \delta = 0.03$  at 140 Kv/cm,  
PMN:PT 90/10 with  $\epsilon = 1,100$   $\tan \delta = 0.01$  at 140 Kv/cm,  
PLSnZT with effective slope capacitance equivalent to  $32 \mu\text{f}/\text{cm}^2$  at 75 Kv/cm and a working voltage of 1 volt. For the PZT and PMNPT compositions the microwave test chips comprise two classes of test structure, a simple parallel plate capacitor and a microstrip loaded with a pair of parallel plate capacitors. For the PLSnZT switching systems to test the slope capacitance a rapid discharge pulse switching system is being constructed.

Current studies are focused upon La:Nb modified 52:48 PZTs, new relaxor compositions in the PLT and PLZT families, modifications to the PSnZT antiferroelectrics to reduce the separation of forward:backward switching and to eliminate temperature dependence in the backward switching field strength.

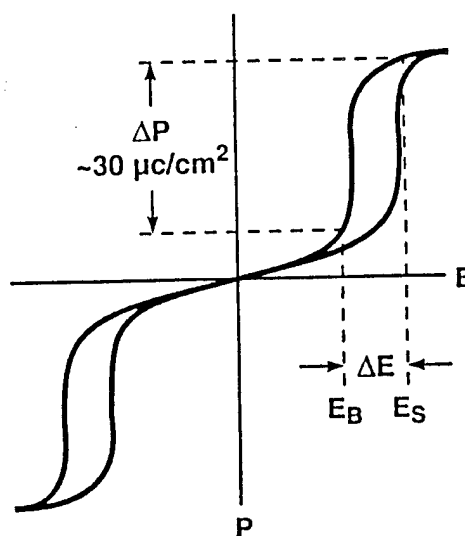
We believe that the phase switching systems offer the potential for a revolution in high capacitance density with volumetric efficiencies up to  $1 \text{ farad}/\text{cm}^3$ .



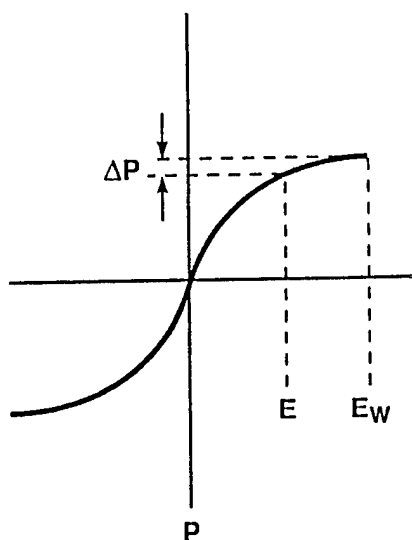
# TYPICAL RESPONSE OF DIELECTRIC MATERIALS FOR DECOUPLING FUNCTION



**FERROELECTRIC**  
(Example: PZT)



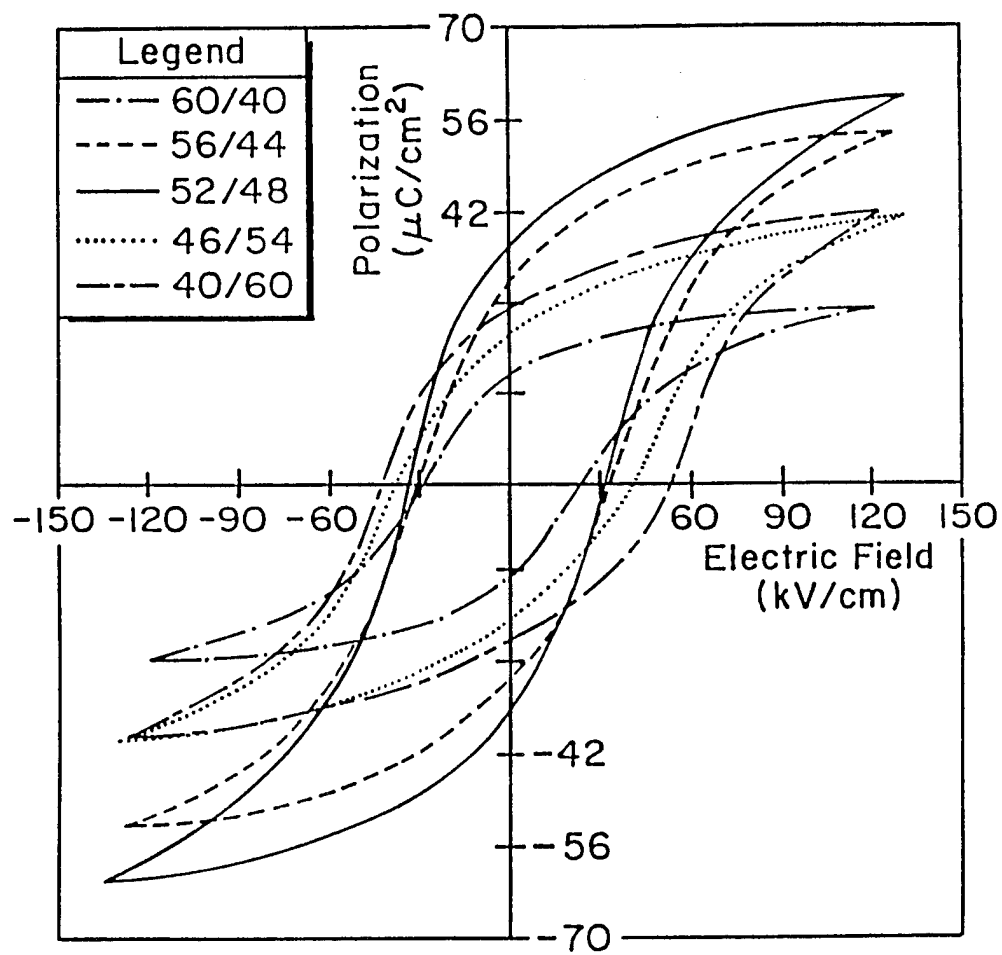
**ANTI-FERROELECTRIC**  
(Example: PSnZT)



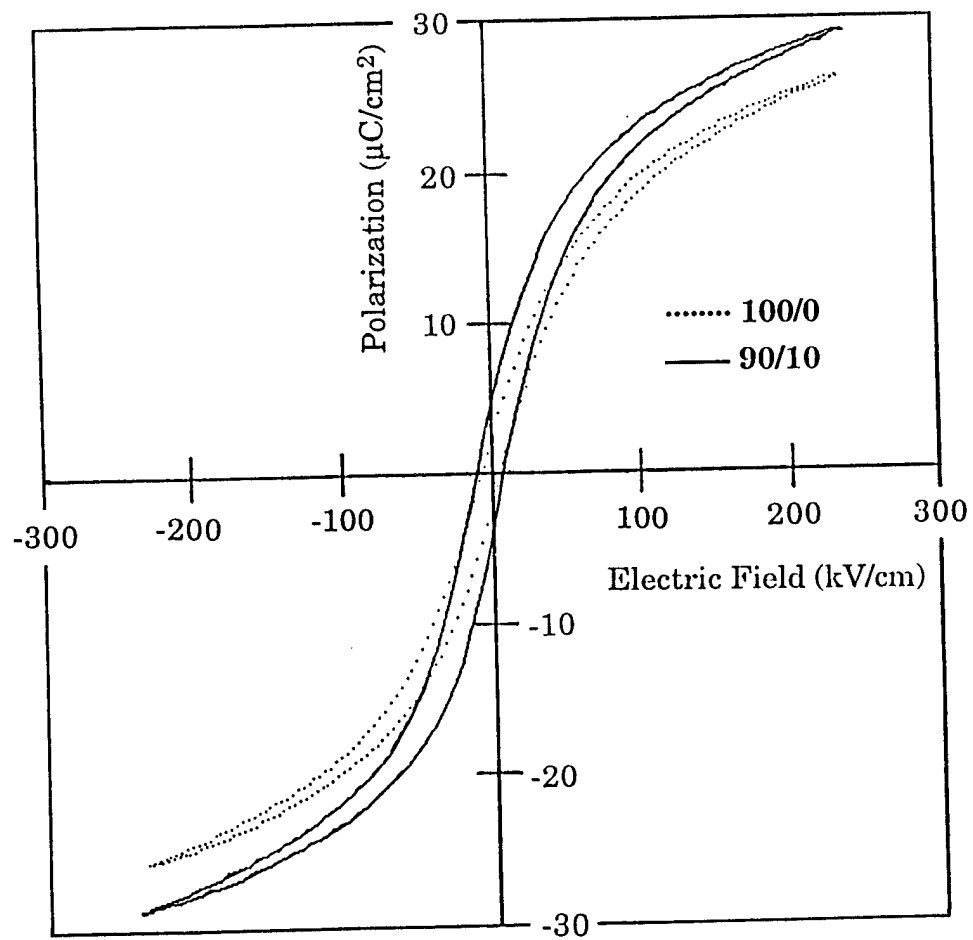
**RELAXOR DIELECTRIC**  
(Example: PMN-PT)

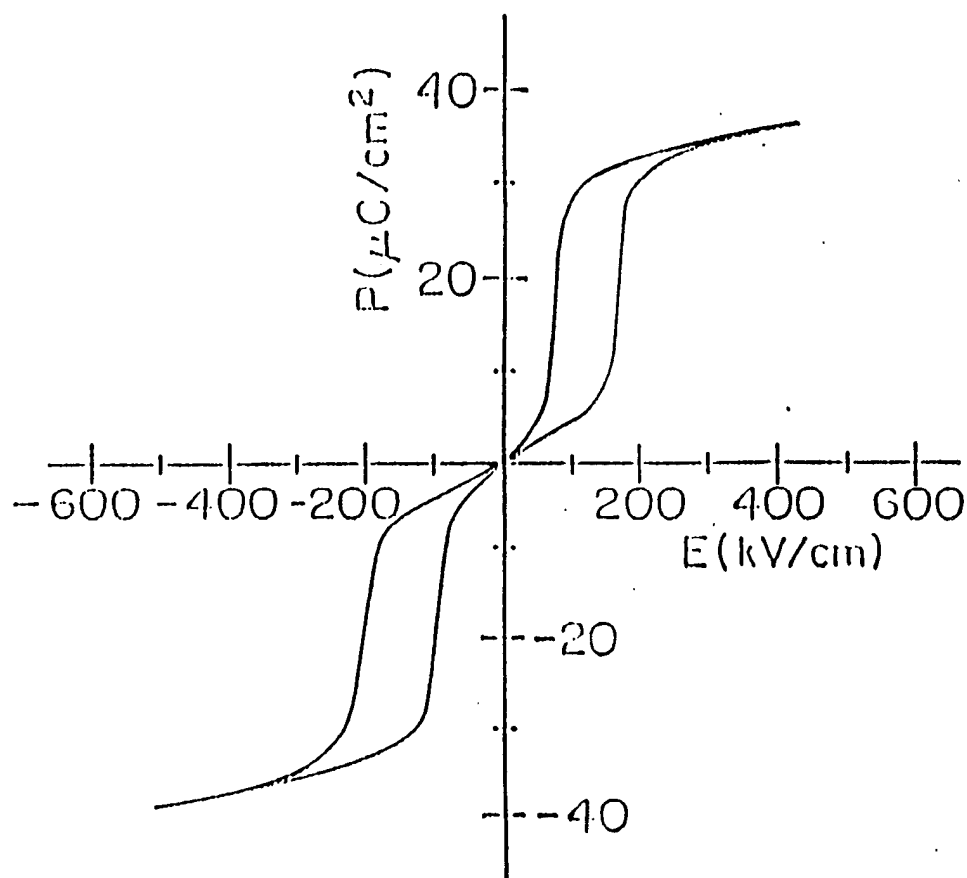
P = CHARGE PER UNIT AREA  
WHERE: E = APPLIED FIELD (Voltage)

## PZT Thin Films



## PMN:PT Thin Films





Square hysteresis response in a thin film of phase-switched Nb-doped PSnZT. Thickness = 0.45  $\mu\text{m}$

$$P_{\text{max}} = 38 \mu\text{C}/\text{cm}^2, P_s = 30 \mu\text{C}/\text{cm}^2$$

$$E_F = 175 \text{ kV}/\text{cm}, E_A = 75 \text{ kV}/\text{cm}$$

$\Delta F \Rightarrow F$  BACK SWITCHING.

0.6 Volt change  $\Rightarrow 20 \mu\text{c}/\text{cm}^2$  charge.

EFFECTIVE CAPACITANCE  $C = 35 \mu\text{F}/\text{cm}^2$

FILM 0.45  $\mu\text{m}$  thick.

CAPACITANCE VOLUMETRIC EFFICIENCY 0.3 FARADS/ $\text{cm}^3$

# SUMMARY

- FABRICATED A RANGE OF COMPOSITIONS IN THE SIMPLE PROPER FERROELECTRIC, RELAXOR FERROELECTRIC, AND PHASE SWITCHING ANTIFERROELECTRIC FAMILIES BY THE SOL-GEL SPIN-ON TECHNIQUE

- SIMPLE PROPER FERROELECTRIC:  
TYPICALLY,

$$\begin{array}{lll} \text{PZT(52/48):} & \epsilon_r = 1010 & \tan\delta = 0.04 \\ & P_r = 28 \mu\text{C}/\text{cm}^2 & E_c = 46 \text{ kV}/\text{cm} \end{array}$$

- RELAXOR FERROELECTRIC (SPIN GLASS) SYSTEM:

$$\begin{array}{lll} \text{PMN:} & \epsilon_r = 2740 & \tan\delta = 0.02 \\ & P_{\max} = 27 \mu\text{C}/\text{cm}^2 & \end{array}$$

- PHASE SWITCHING ANTIFERROELECTRIC:

— "SQUARE" HYSTERESIS RESPONSE IN THE ORTHORHOMBIC Nb-DOPED TERNARY

$$\begin{array}{ll} P_{\max} = 40 \mu\text{C}/\text{cm}^2 & \\ E_{\text{AFE} \rightarrow \text{FE}} = 175 \text{ kV}/\text{cm} & E_{\text{FE} \rightarrow \text{AFE}} = 75 \text{ kV}/\text{cm} \end{array}$$

- CAPACITANCE DENSITY =  $32 \mu\text{F}/\text{cm}^2$  AT  $E_{\text{FE} \rightarrow \text{AFE}}$
- CAPACITANCE VOLUMETRIC EFFICIENCY =  $1 \text{ F}/\text{cm}^3$
- SWITCHING OBSERVED DOWN TO  $0.15 \mu\text{m}$
- La-DOPED TERNARY: